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16. ABSTRACT

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In the review of PAH sampling methods, collection of both gaseous and particulate bound PAH was determined to be necessary to accurately characterize health effects of PAH in ambient air. Most studies have used filters to sample particulate-bound PAH and absorbents to collect vapor phase PAH. The major sampling problems encountered in these studies were PAH losses due to volatilization and reactivity.

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REVIEW OF SAMPLING AND ANALYSIS METHODOLOGY FOR POLYNUCLEAR AROMATIC COMPOUNDS IN AIR FROM MOBILE SOURCES

by

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature of processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of increasing significance to EPA. The state-of-the-art survey of sampling and analytical methodology presented in this report provides an initial step toward measurement of, and understanding the extent of human exposure to, an important class of chemicals -- the polynuclear aromatic compounds -- in air.

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ABSTRACT

The objective of this program was to review and recommend test compounds and sampling and analysis methods for a future EPA study of polynuclear aromatic hydrocarbons (PAH) in microenvironments.

A literature survey was performed by a computer search of nine data bases: Chemical Abstracts (1967-1983), Enviroline (1971-1983), Pollution Abstracts (1970-1983), APTIC (1966-1978), NTIS (1964-1983), Engineering Index (1970-1983), BIOSIS (1970-1983), Excerpta Medica (1970-1983), and Medline (1970-1983). Additional materials representing state-of-the art practice were also reviewed.

Review of PAH profiles in ambient air indicated that concentrations of PAH were generally higher in winter than summer and varied with climate and between sampling sites within an urban area. Levels of several PAH were found to be proportional to traffic density. Studies of the biological activity of ambient air samples showed that some PAH and their nitrated derivatives are extremely carcinogenic and mutagenic. The following compounds were determined to be the most prevalent and mutagenic or carcinogenic in ambient air and were recommended for the future EPA study: phenanthrene, pyrene, cyclopenta(c,d)pyrene, benzo(a)pyrene, dibenz(a,h)anthracene, 1-nitropyrene, fluoranthene, benz(a)anthracene, benzo(e)pyrene, benzo(g,h,i,)perylene, coronene, and 3-nitrofluoranthene.

In the review of PAH sampling methods, collection of both gaseous and particulate-bound PAH was determined to be necessary to accurately characterize health effects of PAH in ambient air. Most studies have used filters to sample particulate-bound PAH and adsorbents to collect vapor phase PAH. The major sampling problems encountered in these studies were PAH losses due to volatilization and reactivity. A modified high volume (Hi-Vol) sampler which can remove large particulates (>10 μm) and collect both particulate and vapor phase PAH was recommended for the EPA study.

Both screening and analytical methods for PAH determination were reviewed. Luminescence techniques, thin layer chromatography, ultraviolet (UV) spectroscopy, and a fluorescence spot test have been successfully applied in previous PAH screening studies and were recommended for the EPA study. For PAH analysis, combined gas chromatography/mass spectrometry (GC/MS) with either electron impact or negative ion chemical ionization was found to provide higher sensitivity and specificity than other techniques reviewed and, despite the high cost, was recommended for the future study.

This report was submitted in fulfillment of Contract 68-02-3487 by Battelle Columbus Laboratories under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from March 1, 1983 to September 30, 1983, and work was completed as of November 30, 1983.

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LIST OF ABBREVIATIONS

BAP	benzo(a)pyrene
BEP	benzo(e)pyrene
BKF	benzo(k)fluoranthene
CI	chemical ionization
EI	electron impact
FID	flame ionization detection
FLNS	fluorescence line narrowing spectrometry
FT	Fourier transform
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
HI-VOL	high volume sampler
HPLC	high performance liquid chromatography
HR	high resolution
IR	infrared
LO-VOL	low volume sampler
MS	mass spectrometry
NCI	negative ion chemical ionization
NMR	nuclear magnetic resonance
PAH	polynuclear aromatic hydrocarbon
RTP	room temperature phosphorimetry
SF	synchronous fluorescence
SIM	selected ion monitoring
SL	synchronous luminescence
TLC	thin layer chromatography
UV	ultraviolet
XEOL	X-ray excited optical luminescence

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SECTION 1

INTRODUCTION

The Methods Development Branch is developing sampling and analytical methodology for an experimental study of human exposure to polynuclear aromatic hydrocarbons (PAHs) and PAH derivatives in ambient air within microenvironments, emphasizing those which originate from mobile sources. The form and concentration in which these PAH materials appear in microenvironments are matters of increasing interest and importance because of the increasing use of diesel powered vehicles. Of particular concern is the presence of nitrated PAHs in diesel exhaust. PAHs, especially pyrene, have been reported to react readily with nitrogen oxides to form nitrated derivatives, which are powerful direct acting mutagens. Both the PAHs and nitrogen oxides are present in combustion emissions; thus the formation of nitroaromatics in these emissions or in subsequent atmospheric reactions is possible. In recent studies conducted by Battelle Columbus Laboratories, nitrated PAHs have been identified in urban air particulate samples. Reliable sampling and analytical techniques need to be established before potential effects of PAHs and PAH derivatives on the environment can be assessed.

The specific objectives of this project were to survey and review the current knowledge of PAHs found in ambient air and to use the results of the review to develop a design and analytical methodology for an experimental study of human exposure to PAH found in ambient air within microenvironments.

The first phase of this project is a review of the available literature to determine:

- Sampling and analysis methodology for PAHs in ambient air
- Specific PAH compounds and subclasses of the PAHs that are potentially most important because of their long-term health risk
- PAH profiles from specific mobile sources that can be used to relate the PAH concentrations in air to those sources.

A literature survey was performed by a computer search of nine data bases:

Data Base	Years Searched
Chemical Abstracts	1967-1983
Enviroline	1971-1983
Pollution Abstracts	1970-1983
APTIC	1966-1978

Data Base	Years Searched
NTIS	1964-1983
Engineering Index	1970-1983
BIOSIS	1970-1983
Excerpta Medica	1970-1983
Medline	1970-1983

Because the citations obtained from Chemical Abstracts listed only the authors and topics, a manual search of the abstracts of those topics of interest was performed. To collect information that might have been missed in the computer search, a manual review was also conducted of other sources considered to represent current state-of-the-art practice, such as handbooks, manuals, and research reports published by the U.S. EPA and recognized professional organizations. Over 1000 citations were obtained as a result of both computer and manual searching. Abstracts and citations considered most relevant to the subject area were reviewed and divided into two subsets, sampling methods and analysis methods, for further evaluation. Photocopies of some important articles were obtained to allow for a more critical review than abstracts alone provided.

The results of this review are presented in the following three sections:

- PAH profiles and biological activity from ambient air samples
- Sampling methodology for the collection of PAHs
- Chemical analysis methodology.

The relative importance of PAHs that are found in ambient air and that originate from mobile sources, in terms of their long-term health risk, is addressed in the first section. Sampling, analytical and screening methodologies for the measurement of PAHs and PAH derivatives that may be suitable for a U.S. EPA proposed experimental study are identified and evaluated in the other two sections. These methodologies will be used to guide the development of an experimental plan for a human exposure study.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Several important characteristics of PAH profiles in ambient air and their biological activity have been identified in this review. PAH concentrations in ambient air vary widely and in general are higher in winter than in summer. The concentrations of PAH compounds also vary between sampling sites within an urban area and vary with climate. However, levels of several PAHs such as cyclopenta(c,d)pyrene, benzo(g,h,i)perylene, and coronene are directly proportional to traffic density. These compounds can be used, therefore, as indicators to identify the origin of mobile source contamination within microenvironments. Based on these characteristics, such compounds should be considered for monitoring in the EPA experimental study.

Several carcinogenic and mutagenic PAHs and PAH derivatives found in ambient air should also be investigated in the EPA study. Benzo(a)pyrene, benzofluoranthenes, cyclopenta(c,d)pyrene and dibenz(a,h)anthracene are known carcinogens and therefore should be considered important compounds to be monitored in the future study.

Nitropyrenes and nitrofluoranthenes are potent direct-acting mutagens and have been identified in both ambient air and automobile exhaust. Dinitropyrene and hydroxynitropyrene are two materials with the highest mutagenicity known to date and have been found in mobile source emissions. While these two compounds have not yet been found in ambient air, they will probably be found in microenvironments polluted by these sources.

Based on the available information, the following PAH compounds are potential candidates to be monitored in the EPA experimental study:

phenanthrene
fluoranthene
pyrene
benz(a)anthracene
cyclopenta(c,d)pyrene
benzo(e)pyrene
benzo(a)pyrene
benzo(g,h,i)perylene
dibenz(a,h)anthracene
coronene
1-nitropyrene
3-nitrofluoranthene
benzofluoranthenes
indeno(1,2,3-c,d)pyrene

Monitoring for the above species would provide a general characterization of PAH concentration in ambient air. The measurement of these compounds can be used to assess the PAH profile in a wide variety of microenvironments, including those containing emissions from mobile and stationary sources. Furthermore, the same compounds can be used to assess the PAH concentration within residential sites. For this application, it would be highly desirable to correct for PAH contributed by tobacco smoke. This correction can be made, if a correlation exists between PAH compounds and several tobacco smoke products such as quinoline and isoquinoline. If such a correlation exists, then an adjustment of the PAH concentration due to tobacco smoke can be made. Thus, by including tobacco smoke marker compounds in the list of compounds to be monitored, residences and work places can be included as microenvironments.

Sampling methods used in the EPA future study must collect representative samples of potentially harmful PAHs in ambient air and must also minimize sampling losses frequently encountered with PAHs. PAHs exist in vapor and particulate phases in the atmosphere, and most particle-bound PAHs are found in the submicron range. These small particles also produce a major percentage of the mutagenic activity of airborne particulate matter (43,45). Both the vapor and respirable particle-bound PAHs should be considered for collection, and an appropriate sampling and analysis system should be designed for the experimental study.

PAH losses in sampling are mainly due to volatilization and reactivity with NO_2, O_3, and UV radiation. Volatilization of PAHs cannot be avoided, but can be minimized by the use of back-up traps in the sampling system for collection of vapor phase material. Some reactive PAHs are believed to undergo atmospheric reaction, such as nitration, to convert PAHs to nitro PAHs. Erroneous results will occur if these reactions continue during the sampling and analysis procedure. In general, reactivity mechanisms of PAHs in the atmosphere are not well defined, and a simple solution to eliminate reactivity losses in sampling has not yet been demonstrated. A device to remove O_3 and NO_2 prior to particle sampling should be considered to minimize this degradation.

The recommended sampling device for the EPA experimental study is a modified Hi-Vol sampler. With a properly designed sampler inlet, a modified sampler can remove larger particles (>10 μm) before passage of the air sample through the collection system. The collection system should consist of a filter medium to collect particulate matter and a solid sorbent cartridge to trap vapors. Proper sampling procedures need to be designed and validated to avoid volatilization losses and reduce reactivity problems.

The procedures to be developed should consider the following parameters:

- Sampler configuration
- Sampling time
- Sampling temperature
- Sampling flow rate
- Filter face velocity
- Frequency of samples
- Quantity of sample necessary for measurement

Once ranges have been established, the operation of samplers can be optimized for the specific site selected.

Rapid screening methods for PAHs identified in this review include a sensitized spot test, UV spectroscopy, TLC with fluorescence and/or UV detection, and luminescence techniques.

Several analytical techniques such as HPLC with UV and/or fluorescence detection, GC/FID, and GC/MS have been used successfully to measure PAHs in ambient air and can be considered for the EPA experimental study. The HPLC technique is very sensitive and less expensive than GC/MS technique. It may be possible to determine PAHs using HPLC methods without sample cleanup. If so, it may be possible to perform HPLC analyses in the field. No reference has been found describing the use of synchronous fluorescence (SF) detection with HPLC for the determination of PAHs in air. This technique offers several advantages in terms of improved sensitivity and specificity. Therefore, development and evaluation of synchronous fluorescence detection with HPLC is also suggested for the future study. It should be noted that single column GC or HPLC analyses employing single detectors do not give unambiguous results, and confirmation of these analytical results with specific techniques such as GC/MS is necessary.

Capillary column GC/FID has been demonstrated to be useful as a routine analytical tool for PAH determinations. A sample cleanup procedure is required to remove the interference from aliphatic hydrocarbons. Few analytical methods for detection of nitro PAHs are reported in the literature. The negative ion CI GC/MS technique is very sensitive, but requires the use of expensive and sophisticated equipment. Therefore, less expensive methods such as GC and/or HPLC techniques should be developed and evaluated for the determination of nitro compounds in the future study. In the future EPA experimental study--for the most important sample types, which demonstrate unusually high mutagenicity and/or carcinogenicity -- more sophisticated analytical techniques (such as EI GC/MS and NCI GC/MS) will be required to provide a more complete chemical characterization.

SECTION 3

POLYNUCLEAR AROMATIC HYDROCARBON PROFILES AND BIOLOGICAL ACTIVITY FROM AMBIENT AIR SAMPLES

AN OVERVIEW OF PAH PROFILES IN AMBIENT AIR

Considerable information[1-39] is available in the literature describing the profiles* of PAHs from various sources in ambient air particulate material. The results of a literature survey indicate that PAHs in ambient air are generally found in greater amounts in winter than in summer. Only one reference[1] cited conflicting results that coronene and 1,2,3,4-dibenzopyrene in heavy traffic were relatively more abundant in summer than in winter. The increased PAH concentrations in winter are mainly due to emissions from residential heating systems, and the low summer concentrations of PAHs may be due to photochemical degradation and/or sample loss from higher sampling temperatures. Valori and coworkers[12] analyzed samples collected from polluted air in Rome. These researchers observed that the highest PAH levels occurred in winter months during morning rush hours. They attributed the PAH to domestic heating and automotive traffic.

Another general trend observed was that the benzo(a)pyrene (BaP) concentrations in air particulate matter appear to have declined in the past several years. Faoro and Manning[2,3] investigated BaP and benzene-soluble fraction (BSO) concentrations in ambient air particulate material collected by the National Air Surveillance Network (NASN) for the 1960-1977 period. The data indicated that concentrations of BaP and BSO declined consistently from 1960-1977 at most of the urban and background sites studied. For example, average BaP concentrations declined about 50 percent, from 4 ng/m^3 in 1967 to 2 ng/m^3 in 1972. The authors concluded that local open burning ordinances, auto mobile emission controls, and decreasing coal usage are probable factors contributing to the observed trend. It is possible that the large changes in analytical methodology over this period may also have contributed to the apparent decline in BaP and BSO concentrations.

Another observation of this survey was that the concentrations of individual PAHs obtained from different sites varied widely, from 0.1 ng/m^3 to 100 ng/m^3. Several studies[4,10] have been conducted in Japan to evaluate the PAH content in ambient air of various Japanese cities. In some

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*The term profile in this report represents the value of the concentrations of individual PAHs and/or the relative values of the concentrations of individual PAHs vs time or location in a sample.

studies,[4,6] average BaP concentrations in Osaka air (1968-1969) were found to be 30-60 ng/m^3, which is much higher than the concentrations found in American cities. The concentration of BaP decreased to 24 ng/m^3 in Osaka in 1970.[7] The characteristic seasonal concentration variation (high winter/low summer) was also observed in these studies. One study[5] indicated that BaP concentrations in the commercial district of a Japanese city were 14.0 ng/m^3 in winter, 9.4 ng/m^3 in autumn, 5.7 ng/m^3 in spring, and 2.7 ng/m^3 in summer. In another study,[10] average BaP concentrations within the city of Wakayma were found to be 4.6 ng/m^3 in residential areas, 5.0 ng/m^3 in industrial regions, and 1.6 ng/m^3 in agricultural areas. Several studies[14-22] have also been conducted to measure PAHs in the air in other countries. The levels of PAHs measured depended on the sites sampled.

PAH concentrations were observed to vary with different climatic regions. One study[11] was performed to investigate the content of PAHs in air in ten Polish towns situated in different climates. The PAH levels varied during 1966 in the following ranges: BaP, 29-133 ng/m^3; pyrene, 34-167 ng/m^3; benzo(e)pyrene, 14-80 ng/m^3; and benzo(g,h,i)perylene, 34-124 ng/m^3.

CONTRIBUTION OF MOBILE SOURCES TO PAH CONTAMINATION IN AMBIENT AIR

The major emission sources of PAHs are heat-generation sources, such as burning coal, oil, and gasoline; motor vehicle exhaust; and industrial processes. Olsen and Haynes' review[23] showed that heat generation accounts for more than 85 percent of the PAHs in air. Similar conclusions were drawn in a recent review by the National Research Council,[24] that pointed out that data assembled by the U.S. EPA in 1974 led to the estimate that 97 percent of the BaP emitted in the United States could be attributed to stationary fuel combustion. The major contributors are coke ovens, refuse fires, and the inefficient combustion of coal in residential furnaces. Mobile sources are not the major sources of PAH contamination in ambient air. However, in a microenvironment such as a parking lot, underground mine, tunnel, or heavy traffic area, mobile sources may be the main contributors of PAH contamination.

Bosco and coworkers[25-27] determined PAH levels in the atmospheric dust of the city of Siena, Italy. The concentrations of most of the identified PAHs showed a significant decrease when a part of Siena was closed to motor traffic. Since the city of Siena does not have heavy industry, the reduction of automotive traffic was the major reason for the decline of PAHs.

Characterizing the contributions of mobile sources to PAH contamination in the air is complicated. According to the available information in the literature, two methods can be used to identify mobile sources of PAHs in the atmosphere. These methods are choosing characteristic compounds such as cyclopenta(c,d)pyrene, benzo(g,h,i)perylene and coronene as indicators for mobile sources; and using trace materials, such as lead, vanadium, and carbon monoxide as indicators for mobile and non-mobile sources.

Several references[4,28-35] are available on the use of a specific PAH as an indicator for mobile sources. Sawicki and coworkers[28] examined the air of 14 American cities for the following PAHs: pyrene, BaP, benzo(e)pyrene, benzo(k)fluoranthene, perylene, benzo(g,h,i)perylene, anthanthrene and coronene. Based on their experimental data, the ratio of BaP to benzo(g,h,i)perylene was 0.6 and the ratio of BaP to coronene was 1.0 in the following types of samples: automobile exhaust soot from a tailpipe, air from a Cincinnati automobile safety lane, and air from a Cincinnati downtown garage. The same group also demonstrated that BaP concentrations in air particles were elevated in urban and nonurban areas in and around the eastern coal mining belt; for example, the BaP/coronene ratios were in the range of 1.7 to 8.3 for the winter months. The authors proposed that the ratios of BaP to benzo(g,h,i)perylene and to coronene could be used as possible indicators of air pollution due to automobile exhaust fumes or coal combustion pollution. One study[13] showed that the profile of PAHs in Pittsburgh air was similar to those reported by Sawicki for other American cities,[28] with the exception of a high value of benz(a)anthracene (BaA), which ranged from 0.8 to 37 ng/m^3.

A similar study was conducted by a Japanese group,[4] who investigated PAHs in Osaka air. The BaP/benzo(g,h,i)perylene and BaP/coronene ratios for urban air and automobile exhaust followed the same trend observed by Sawicki. This group also suggested that these ratios can be considered as indicators of air pollution sources. Average BaP concentrations were 30-60 ng/m^3, which are considerably higher than the BaP concentrations found in American cities.

Gordon and coworkers[29,30] evaluated the patterns in airborne particulate matter at four Los Angeles sites. The concentrations of coronene correlated well with traffic density. The PAH patterns, normalized to coronene, were similar for three sites and resembled patterns for automotive exhaust previously studied by the same group. The fourth site had a distinctly different pattern, reflecting local sources of non-automotive PAHs. Another study conducted by Katz and Chan[31] showed that in Hamilton, Toronto, and several other Ontario cities, benzo(g,h,i)perylene was the most abundant PAH where motor vehicle traffic was a major source of air pollution. However, BaP represented an important fraction of the PAH content in urban areas where the dominant source was coal combustion.

Suda and coworkers[32] obtained similar results, showing that mobile sources were the major contamination source based on the ratio of the total atmospheric PAH level to the benzo(g,h,i)perylene level. The result is in fairly good agreement with that based on the average PAH levels in automotive exhaust from 26 Japanese cars.

Recently, Masclet and colleagues[33] measured PAHs in the airborne particulate material in Paris, in December 1981 and January 1982. They also observed that the relative abundance of PAHs varied with the main particulate source on each sampling day, i.e., automobile traffic in December and home heating in January. In Sorensen and Vester's study,[34] it was expected that the center of Copenhagen would be polluted mainly with PAHs of high molecular weight, such as benzo(g,h,i)perylene discharged from motor vehicles. However,

the ratio of BaP to benzo(g,h,i)perylene ranged from 0.2 to 4.4, benzo(g,h,i)-perylene was considerably lower than expected, and no correlation was found between the concentrations of PAH in the air of Copenhagen and meteorological data. In addition, one single pollution source could not be identified.

Grimmer and coworkers(35) used BeP measurements as a basis to construct PAH concentration profiles of several areas. Profiles of PAHs from automobile emissions and from measurements in a traffic tunnel were similar, with cyclopenta(c,d)pyrene the most abundant PAH. Cyclopenta(c,d)pyrene can also be an indicator for mobile source contamination.

The use of trace elements such as lead and vanadium to identify sources of pollutants in the atmosphere was described in a recent National Research Council review.(24) Colucci and Begeman(36-38) conducted several studies to determine the contribution by automobiles to the PAHs in the air of cities such as New York, Detroit and Los Angeles. They used tracer elements to identify automotive and non-automotive sources and calculated correlation coefficients of BaP with carbon monoxide (CO) (a motor vehicle tracer), with lead (a gasoline vehicle tracer), and with vanadium (an oil tracer). Vanadium concentrations were two times higher in winter than in summer, indicating that the higher amount of BaP was contributed by the combustion of residual fuels used for heating. In another study(39) of air pollution from automobile exhaust, gases in an underground parking garage were measured. Levels of CO exceeding 200 ppm were recorded and indicated that CO levels can be an indicator for mobile source contamination.

BIOLOGICAL ACTIVITY OF AMBIENT AIR SAMPLES

The biological activities of PAHs and their derivatives present in ambient air, diesel exhaust and other sources have been reviewed by the National Research Council in 1972,(40) 1981,(41) and 1983(24) and by the World Health Organization in 1973.(42) Evidence has shown some PAHs, such as BaP, and their derivatives to be carcinogens and/or mutagens.

The Ames Salmonella/mammalian microsome assay has provided a rapid cost-effective *in vitro* screening method for mutagen detection and has been the major mutagenicity assay utilized to evaluate samples of air particulate material. The application of this assay with multiple tester strains, used in the presence and absence of a metabolic activation system, can provide an initial characterization of potential carcinogens present. For this reason, the discussion of this section emphasizes only the studies using the Ames bioassay.

Characterization of Mutagenic Activity in Air Particulate Matter

Similarities in the mutagenicity of air particulate material from different sites have been demonstrated in several studies. For example, two studies(43,44) have shown that the greatest mutagenicity of air particulate

matter is in the smaller particle size range, below 10 µm. Several investigators[45,46] have shown that both metabolically-activated and direct-acting mutagenic compounds are present in air particulate matter. These authors agreed that PAHs are not the major mutagenic factors associated with air particulate matter. In addition, they have shown that air particulate matter is more mutagenic at industrial and urbanized sites than at rural sites.

Recently, Flessel and coworkers[47] compared the mutagenicity of air samples from sites in Contra Costa County, California with different degrees of industrialization and cancer rates. Contra Costa County is one of 39 counties in the U.S. that have been shown to have high cancer mortality rates. These studies all indicated a higher mutagenic activity in samples from the more urbanized or industrialized sites. However, detailed later studies found there was no identifiable effect on cancer risk from air pollution in the county.[47a]

In a year-long study at a Chicago school site, Commoner and colleagues[48] showed that a major parameter affecting airborne particulate mutagenicity was the wind direction. In this study, a plot of wind directions versus relative mutagenic activity showed that wind directions of either northwest or east produced air particulate samples with the greatest mutagenicity. Moller and Alfheim[49] studied the mutagenicity of airborne particles from two locations in Oslo over a three-month period. They observed higher mutagenicity in February (i.e., during the heating season) than in March and April. They also reported that meteorological conditions may influence the mutagenicity levels; for example, the mutagenicity (revertants/cm^3 of air sampled) was highest on cold clear days with little wind.

In certain cases, studies can be designed to identify specific emission sources that contribute to the mutagenicity of the ambient particulate organic matter. Moller's group[50] conducted another study on the mutagenicity of airborne particles in relation to traffic and air pollution parameters such as CO, NO_x, and PAHs. The results indicated that the mutagenicity of daytime street-level samples, that originated in motor vehicle exhaust in an area with dense traffic, was 4-20 times higher than that of simultaneously collected samples at roof level or in the park. Furthermore, the mutagenicity at street level varied with traffic density, while the activity of samples from roof level and from the park showed no such correlation. Lewtas[51] also compared the mutagenic activity of organic compounds from particles of less than 1.7 µm diameter collected at Los Angeles freeway sites, both upwind and downwind. The particles collected downwind, presumably from the automobiles and trucks on the freeway, were significantly more mutagenic than those collected upwind originating from the Pacific Ocean. These authors agreed that both gasoline and diesel engine exhaust from automobiles, buses, and trucks contribute to the mutagenicity of ambient air particles.

Recently, nitrated PAHs have been identified in extracts of particulate material from diesel engine exhaust and urban air. Several of these nitrated PAHs are strong direct-acting mutagens in Salmonella tests,[52-56]

and are carcinogenic in animal experiments[57] as well as mutagenic in test systems using mammalian cells.[58]

Certain nitrated PAHs (e.g., 1,8-dinitropyrene) are extremely potent frameshift bacterial mutagens. Concern was expressed by Rosenkranz and coworkers[59] that bacterial mutagenesis assays may overestimate the mutagenicity of nitrated PAHs in diesel emissions. The importance of evaluating the mutagenic activity of these emissions in eucaryotic organisms, mammalian cells and whole animals was emphasized. Lewtas[58] conducted a review to compare the microbial mutagenicity, mammalian cell mutagenicity, and mouse skin tumorigenicity of the extractable organic compounds from diesel particles. The results indicated that there is generally good agreement among the bacterial mutagenesis assays, mammalian cell assays, and skin carcinogenesis assays. The author suggested that bacterial mutagenesis assays do not overestimate the mutagenic activity of these nitro PAHs.

Fukino's group[53] studied the mutagenicity of airborne particles in the Ames Salmonella system. The results suggested that emissions from automobiles, home heaters, and power plants may be primary sources of atmospheric direct-acting mutagens. However, secondary direct-acting mutagens may be partly formed by the nitration of PAHs with NO_2 in the atmosphere, because the measured concentrations of BaP and NO_2 were higher in the samples producing the highest direct-acting mutagenicity. Madsen and coworkers[54,55] collected air particulate material at three stations in central Copenhagen with different contributions from automobile exhaust emissions. The three sampling sites were street level, 22 m above street level, and within a hospital zone at street level. Two classes of mutagens were identified: a non-polar extract rich in PAHs as well as other metabolically-activated mutagens and a polar extract containing direct-acting mutagens. Based on the covariance between lead and mutagenicity, the authors suggested that at all stations the mutagenicity of the nonpolar extract was dominated by automobile exhaust products. The polar extract was relatively less influenced by traffic emissions. This may be because the activity of this polar fraction was mainly attributed to non-automotive emissions and/or emissions from stationary sources possibly transformed by atmospheric reactions.

Recently, Pitts[60] investigated the diurnal variations in the mutagenicity of ambient particles collected at the same time at three sites in southern California. At each sampling site five high-volume samplers were run for 24 hours with filter changes every 3 hours, and a sixth sampler was operated for the entire 24 hours without filter replacement. The data showed good agreement between the activities of the experimental 24-hour samples and the estimated 24-hour activities calculated from the corresponding three hour samples. These data suggest that chemical transformations of mutagenic material collected on the filters are either very fast or very slow relative to the time scale used in these experiments. The three hour average mutagenic densities correlated well with CO, NO_x, and lead levels.

In a study by Dehren, Pitz, and Tomingas,[61] a chemical fractionation scheme was used to separate crude air particulate material into cyclohexane and methanol extractable fractions. An alumina column was used to fractionate the cyclohexane extract further into a purified cyclohexane fraction containing PAHs and a 2-propanol fraction containing azo-heterocyclic compounds. The highest mutagenic response was found in the 2-propanol and methanol extracts, neither of which contained PAH compounds.

The combination of a chemical fractionation scheme with an Ames bioassay system has been shown to be an increasingly powerful tool for the identification of potential carcinogens in complex extracts of air particulate material. Battelle[62] conducted a joint study with the U.S. EPA at Research Triangle Park, NC, to develop a fractionation scheme to separate extracts of air particulate matter from Washington, D.C. into acidic, basic, aliphatic, aromatic, moderate polarity, and high polarity fractions. The acidic fraction accounted for about 50 percent of the mutagenic activity with and without activation of the total extracts. Mononitrated PAHs, including nitronaphthalene, nitrophenanthrene isomers, nitrofluoranthene, nitropyrene, and 2,7-dinitrofluorene, were found in the aromatic and polar neutral fractions. The high activity in the acidic fraction indicated that, besides PAHs and nitrated-PAHs, some other types of compounds were present in the extracts of air particulate material that may be strong mutagens and/or carcinogens. Recently, one group[63] reported that a strong mutagen, hydroxynitropyrene, was present in diesel exhaust extracts. Because of the acidic properties of the hydroxy group, these types of compounds may be present in the acidic fraction of the extracts of air particulate material and contribute to the mutagenicity. So far, no study has been performed to characterize these types of compounds in air particulate material, and it would be worthwhile to pursue such studies.

Several limitations to data interpretation were identified in the mutagenicity studies. Air particles are complex mixtures and may contain hundreds of compounds. In such a complex matrix, effects which inhibit or increase the mutagenicity of an individual compound may occur. The mechanisms for these effects are being studied.[64-66] Toxicity of compounds in the complex mixture, as well as the nature or composition of the mixture itself, can mask mutagenicity. Artifacts generated by sampling procedures and sample handling can lead to erroneous results. Huisingh and coworkers[67] have shown that extracts of particulate material from diesel exhausts are more mutagenic when extracted with dichloromethane than with cyclohexane. This group also demonstrated a 50 percent loss of mutagenic activity as well as an increase in toxicity for the extract upon storage (2 months at 4°C). In general, quinones and ketoaromatics are toxic but not mutagenic. It is possible that nitroaromatics may have originally accounted for a larger percentage of the activity, but with storage, many of the nitroaromatics may have been oxidized to quinones and ketoaromatics.

The results of a Battelle study[62] supported this postulate in that the measured mutagenic activity of the stored diesel exhaust extract decreased significantly while the toxicity increased over the two-year storage.

Furthermore, it was demonstrated that the 1-nitropyrene concentration decreased about 75 percent during this storage. For the other identified nitro PAHs, half showed at least a 75 percent loss in concentration during the storage period. It is recommended, therefore, that a standard procedure for sample storage and handling be formulated and instituted. Post-collection reactions cannot be eliminated, but by using standardized procedures can be minimized.

SELECTION OF PERTINENT PAHS AND DERIVATIVES FOR AN EPA EXPERIMENTAL EXPOSURE STUDY

Based on the available information about PAHs and their derivatives present in air particulate matter, the following compounds are potential candidates for measurement in the EPA experimental study of human exposure to mobile source emissions found in ambient air within microenvironments:

- Pyrene
- Fluoranthene
- 1-Nitropyrene
- 3-Nitrofluoranthene
- Benz(a)anthracene
- Coronene
- Chrysene
- Cyclopenta(c,d)pyrene
- Benzofluoranthenes
- Benzo(e)pyrene
- Benzo(a)pyrene
- Benzo(g,h,i)perylene
- Indeno(1,2,3-c,d)pyrene
- Dibenz(a,h)anthracene
- Dinitropyrenes
- Dinitrofluoranthenes
- Hydroxynitropyrenes

A recent study by Grimmer and his group[68] showed that PAHs with more than three rings accounted for a large percentage of the total carcinogenicity in crankcase oil, automobile exhaust condensate and flue gas condensate as shown by the mouse-skin painting test. Similar results obtained by another group[69] indicated that PAHs with four to six rings showed the strongest experimental carcinogenicity. The experiments were conducted by subcutaneous injection of extracts of automobile exhaust condensates, coal furnace emissions and air-borne particles, and different fractions of these extracts. The same trend was also reported in several review articles.[24,43] For this reason, we suggest that emphasis should be placed on PAH with four or more rings in the experimental study.

Both pyrene and fluoranthene, in relatively large amounts compared to other PAH species, are found in air particulate matter and automobile exhaust emissions. These compounds do not show carcinogenic activity, but have some mutagenic activity in *in vitro* animal tests.[24] Their derivatives, such as nitrated pyrene and fluoranthene, are strong direct-acting mutagens and both nitro compounds are present in extracts of air particulate material[62] and diesel exhaust emissions.[71] These compounds are typically present, however, at 0.01 to 0.1 times the levels of their parent PAHs. At this point, the measurement of parent compounds is as important as is the measurement of their nitro derivatives for the experimental study. This is particularly true if a correlation can be obtained between the parent compounds and their nitro

derivatives. It may be possible to infer the nitro PAH concentration based on the measurement of parent compounds within the environment that is monitored.

Recently, Battelle(62,71) performed a joint study with the U.S. EPA in which both 3-nitrofluoranthene and 1-nitropyrene were detected and quantified in extracts of diesel exhaust particulate material, but the levels of 1-nitropyrene were 10-20 times greater than the levels of 3-nitrofluoranthene. It is noteworthy that 1-nitropyrene and 3-nitrofluoranthene were both detected and quantified in extracts of ambient air particulate matter, but the 3-nitrofluoranthene was present at levels approximately equal to or greater than the levels of the 1-nitropyrene. This concentration difference between diesel exhaust and ambient air samples suggests that 3-nitrofluoranthene is either more stable than 1-nitropyrene or is more readily formed through atmospheric transformation reactions than 1-nitropyrene. In at least one bacterial mutagenesis test strain, TA98, 3-nitrofluoranthene elicited twenty-five times the mutagenic activity level of 1-nitropyrene. Considering the relative concentration levels and the relative mutagenicity levels, 3-nitrofluoranthene may be the more significant nitro PAH for monitoring in ambient air.

The 1,3-, 1,6-, and 1,8-dinitropyrenes are strong direct-acting mutagens, with the 1,8- species being the most potent. The presence of these compounds in diesel exhaust extracts has been confirmed by several studies.(72,73) Pedersen and Siak (73) estimated that 15-20 percent of the total mutagenic activity of the extract may be contributed by these dinitropyrenes, in addition to as much as 24 percent contributed by 1-nitropyrene. So far, no evidence has been shown that dinitropyrenes are present in extracts of ambient air particulate material. The presence of dinitrofluoranthenes in either diesel exhaust or air particulate materials has not been reported in the literature. It is likely that dinitrofluoranthenes are present in diesel exhaust. More studies are needed in this area.

Recently, one group reported that hydroxynitropyrene had mutagenicity equivalent to that of the dinitropyrenes and was identified in diesel exhaust emissions.(74) It is essential to investigate whether hydroxynitropyrene is present in ambient air particulate material.

Benz(a)anthracene (BaA) and chrysene are both present in air particulate matter and automobile exhaust. These compounds are also carcinogenic in mouse skin tests. Furthermore, the methyl derivatives of these compounds (e.g., 6-, and 7-methyl BaA, 5-methylchrysene) have strong carcinogenic activity. We suggest that BaA and chrysene be monitored in the EPA experimental study. If an unusually high amount of BaA and chrysene were found in a sample from a polluted microenvironment, it would be worthwhile to search for the highly carcinogenic methyl and/or dimethyl derivatives of these compounds.

Cyclopenta(c,d)pyrene is a known carcinogen and also has strong mutagenic activity. Benzo(g,h,i)perylene and coronene are either weak carcinogens or noncarcinogens. These three compounds have been identified in ambient air. Furthermore, according to the PAH profile which was discussed on

pages 7 and 8, these compounds may be indicators for mobile source contamination. For this reason, these three compounds are considered important in the pilot study.

Benzofluoranthenes and benzo(e)pyrene occur in both ambient air and automobile exhaust emissions. In repeated skin paintings, benzo(b)fluoranthene produces skin tumors in mice, and benzo(j)fluoranthene causes a high incidence of skin carcinoma. Benzo(e)pyrene has shown a weaker response than either benzo(a)pyrene or dibenzo(a,h)anthracene in the skin painting experiments in mice, and it appears to be a weak carcinogen. One study[24] indicated that repeated application of the weak carcinogen BeP to mouse skin three times weekly with the carcinogen BaP resulted in a cocarcinogenic effect, which enhances remarkably the carcinogenicity of BaP. In addition, BeP is relatively more stable than BaP and can be used as a reference compound to generate PAH concentration profiles.

Benzo(a)pyrene is present in ambient air as well as in mobile source particulate matter. BaP is a known carcinogen and has indirect-acting mutagen activity (with S9 activation). It is an important compound to be studied.

Dibenz(a,h)anthracene has shown carcinogenic activity, and small doses of dibenz(a,h)anthracene have a greater tumor promoting effect than do comparable doses of benzo(a)pyrene.[75] This compound is also found in ambient air and automobile exhaust. A list of PAHs which are potential candidates for measurement in the experimental exposure study is summarized in Table 1.

TABLE 1. PAH CANDIDATE COMPOUNDS FOR MEASUREMENT IN THE EPA PILOT STUDY

PAH	Molecular Formula (Weight)	Occurrence[a]		Carcinogenic[b] Activity	Relative in vitro[c] Mutagenic Activity	
		Mobile Exhaust	Ambient Air		Animal	Bacteria
Pyrene	$C_{16}H_{10}$ (202)	Y	Y	0	+	0
Fluoranthene	$C_{16}H_{10}$ (202)	Y	Y	0	+	++
1-Nitropyrene	$C_{16}H_9NO_2$ (247)	Y	Y			+++
3-Nitrofluoranthene	$C_{16}H_9NO_2$ (247)	Y	Y			+++
Benz(a)anthracene	$C_{18}H_{12}$ (228)	Y	Y	+	+	++
Chrysene	$C_{18}H_{12}$ (228)	Y	Y	+	+	+
Cyclopenta(c,d)pyrene	$C_{18}H_{10}$ (226)	Y	Y	+	++	++
Benzofluoranthenes	$C_{20}H_{12}$ (252)	Y	Y	++		
Benzo(e)pyrene	$C_{20}H_{12}$ (252)	Y	Y	0/+	+	+
Benzo(a)pyrene	$C_{20}H_{12}$ (252)	Y	Y	++	++	++
Benzo(g,h,i)perylene	$C_{22}H_{12}$ (276)	Y	Y			+
Indeno(1,2,3-c,d)pyrene	$C_{22}H_{12}$ (276)	Y	Y	+		
Dibenzo(a,h)anthracene	$C_{22}H_{14}$ (278)	Y	Y	+	+	+
Coronene	$C_{24}H_{12}$ (300)	Y	Y	+		
Dinitropyrenes	$C_{16}H_8N_2O_4$ (292)	Y	N			++++
Dinitrofluoranthenes	$C_{16}H_8N_2O_4$ (292)	N	N			++++
Hydroxynitropyrenes	$C_{16}H_9NO_3$ (263)	Y	N			++++

(a) Y = Compound occurs in samples from given source.
N = Compounds does not occur in samples from given source.
(b) 0, no tumor; +, tumor in up to 33% of animals, ++, tumors in over 33% of animals.
(c) Benzo(a)pyrene mutagenicity set at ++.

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SECTION 4

SAMPLING METHODOLOGY FOR THE COLLECTION OF POLYNUCLEAR AROMATIC HYDROCARBONS

INTRODUCTION

Ambient air contains a complex mixture of hundreds of compounds present at trace concentrations. In general, the chemical analysis methods are well developed, but the sampling procedures can often reduce the validity of analytical results.[1] In White and Vanderslice's[2] review of polycyclic organic matter (POM), source and ambient concentration sampling techniques were shown to contain uncertainties that limit the usefulness of the data in an environmental assessment of POM. The uncertainties include the possibility of incomplete capture of POM during sampling and the chemical degradation of the collected samples.

The potential for loss of PAHs as a result of volatilization during the sampling process has been recognized by several groups.[3-10] Recently, Battelle[11] conducted a study for the U.S. EPA, to assess the effects of current air filtration sampling methods on the integrity of the collected sample. A detailed literature review was performed to collect information on the volatilization and reactivity of PAHs. The consensus of the articles reviewed is that loss of PAH occurs due to volatilization during the sampling process, but there is not universal agreement as to the magnitude of such losses. Control of sampling temperature and the use of back-up traps can reduce the loss of PAH during ambient air sampling.

Many studies[12-18] have been conducted to evaluate the loss of PAHs through reactions during collection and storage. Recently a Battelle research team[11] has surveyed the literature concerning the reactivity of PAHs. The results indicated that PAHs can undergo chemical transformation when exposed to gases such as NO_2 and O_3, especially in the presence of UV irradiation. The magnitude of this degradation is difficult to assess. In several of these studies,[11,14,15] PAH solutions were spiked onto the surface of glass fiber filters, then exposed to NO_2 and O_3 gases. Since the PAHs studied were not spiked onto ambient particulate material in a manner similar to that of "natural PAHs", the decomposition problem may be more severe than that which would actually occur during sampling. Indeed, some studies[11,17] showed that particle-bound PAHs are more stable than are solvent-spiked PAHs. Recently, Brorstrom's[18] group conducted a series of exposure studies that closely simulated ambient air sampling. The exposure experiments were carried out in a way similar to high volume sampling of atmospheric PAHs. Two high volume samplers were run in parallel and collected ambient air particles for 24 hours. One sampler was equipped with a dosage system to increase the concentration of NO_2, O_3, HNO_2, and HNO_3 during sampling. The other sampler

system was used to determine background PAH measurements in ambient air particulate matter. The results showed that either the addition of NO_2 at 1 part per million (v/v) or HNO_3 at 120 parts per billion (v/v) during ambient air sampling caused degradation of reactive PAHs, such as pyrene, BaA, and BaP, on particles. However, the authors did not mention the exposure sampling temperature at these experiments. Although it was assumed to be ambient temperature, the influence of sampling temperature on PAH degradation was not addressed in these studies. The most pronounced effect was found in the experiment with HNO_3 exposure at 120 ppb. For BaP, the loss was about 95 percent while the concentrations of BaA and perylene decreased by 55 percent and benzo(g,h,i)perylene decreased by 20 percent. Evidence for this degradation was observed when the mononitrated derivatives of these PAHs were tentatively identified. Addition of HNO_2 at 100 ppb had no detectable effect. Since NO and NO_2 are acid anhydrides and form HNO_2 and HNO_3 with water, these results indicate that NO does not react with adsorbed PAHs, but NO_2 does cause PAH degradation which is enhanced by the presence of acids and moisture. The author also indicated that this degradation will probably take place in the atmosphere during transportation with the range of NO_2 concentrations normally found in urban air (0.2 ppm). In the case of O_3 exposure at 200 ppb, degradation was observed in only one of the experiments.

In view of the losses, reactivity and other potential difficulties associated with the collection of PAHs in ambient air, a sampling system for these compounds must be designed to minimize these problems. Specifically, the system should be capable of sampling at a constant flow rate during the sampling interval and providing representative samples with minimal deterioration and contamination. For evaluation of health effects, the sampling system must also generate samples that are truly representative of the air that is actually inhaled by humans. Samples should also be collected in sufficient quantity for the level of detection of the analytical methods and/or bioassay analyses. Consideration of on-site analysis versus sample stability is also important. When on-site analysis is impractical because of the type of sample preparation and equipment required, sample handling and storage should become an integral part of the sampling program. Proper quality assurance procedures should be designed and implemented throughout sampling efforts.

SAMPLE CONSIDERATIONS

Sample Size

In general, two main factors determine the amount of sample to be collected:

(1) The extent to which the environment is polluted
(2) The number and types of analyses required for the sample.

The concentrations of PAHs in ambient air range from less than 1 ng/m^3 in relatively clean air to over 100 ng/m^3 in the polluted air of large cities. Usually a minimum of about 100 m^3 of air must be sampled to collect a sufficient amount of PAHs for chemical analysis. Larger sample sizes are

often needed in order to carry out bioassay analyses. A typical sampling time using a high-volume (Hi-Vol) sampler is 12 to 24 hours.

Sample Type

Polynuclear aromatic hydrocarbons (PAHs) exist in the atmosphere both as vapors and as material either condensed or adsorbed on particles. Generally, the majority of PAHs in the atmosphere are found to be adsorbed on suspended particulate matter with average diameter less than 7 μm, which is in the respirable range. It is important to note that PAHs are strongly associated with particles in the submicron range.(3,19-24)

Miguel and Friedlander(22) found that 75 percent of BaP and 85 percent of coronene were associated with particles having aerodynamic diameters less than 0.26 m, and that one half of the total mass of these compounds was on particles in the size range of 0.075 to 0.12 μm. The mass distribution of coronene and BaP with respect to particle size did not shift with season. A similar study, however, carried out by VanVaeck and VanCauwenberghe(3) indicated that the distribution of the PAHs bonded to particles shifts toward the small particles in winter. In Vu Duc and Favez's study(24) of motor vehicle exhaust in an underground parking lot, more than 80 percent of the PAHs was found to be adsorbed on particles smaller than 1.1 μm. Similar work done by Bjorseth(23) indicated that the largest amounts of PAHs adsorbed on particles were on those of 0.9-3 μm diameter, with less than 1 percent on non-respirable particles (7 μm). Particles of this small size tend to have long residence times in the atmosphere, which may increase the probability of atmospheric chemical and photochemical reactions to produce mutagenic and/or carcinogenic compounds. Therefore small airborne particles should be considered important for collection in the future study.

Only a few studies have been concerned with the collection of vapor phase PAHs, and these studies have produced conflicting results. DeWiest and Rondia(25) measured the particulate matter and gas phase BaP of the Liege aerosol. The reported gas phase BaP concentrations were always less than 15 percent of the total BaP concentrations at air temperatures less than 25°C, but increased to 44 percent at 41°C. Miguel and Friedlander(22) found no measurable pyrene and BaP in the gas phase in Pasadena air. Van Cauwenberghe's group(39) used a Tenax adsorption column mounted after a filtration Hi-Vol sampler to collect gas phase PAHs. Significant amounts of phenanthrene, anthracene, fluoranthene, pyrene, and their methyl derivatives were found in the gas phase.

Recently, a study conducted by Thrane and Mikalsen(4) employed polyurethane foam to collect vapor phase PAHs in a Hi-Vol sampler system. The distributions of PAH on the foam (gas phase) and the filter (particulate bound) agree with the results of the study by VanCauwenberghe(39) previously described. With regard to health effects, the collection of gas phase PAHs in air is as important as the collection of particulate-bound PAHs. Further studies in this area are needed.

In a study by Moller, Alfheim and coworkers,(26) extracts of street and roof level airborne particulate matter showed mutagenic activity only from

particles less than 3 m in diameter. Similar results were obtained by Arashidani's group,[27] who showed that extracts of airborne particles from Japan were mutagenic in Salmonella typhimurium, with the mutagenic response increasing with decreasing particle size. More than 92 percent of the total mutagenic response resulted from extracts of airborne particles less than 10 μm in diameter.

This survey suggests that PAHs exist in the atmosphere in both vapor and particulate phases. Furthermore, most particulate-bound PAHs found in air samples are in the respirable size range (<10 μm), and the major mutagenic activity of extracts of air particulate samples is also in this range. For the future microenvironment air sampling methodology, samples collected for analysis should be representative of the air which is inhaled by the exposed humans. The sampling device should be able to collect both gas and particulate-phase PAHs, with a particle size cutoff less than 10 μm.

SAMPLING DEVICES

The general practice in sampling PAHs in ambient air involves the collection of suspended particulate matter by means of filters or impingers. Vapor phase PAHs have been collected on absorbent materials such as XAD-2, Tenax, and polyurethane foam. This section describes the devices which have been used for ambient air sampling.

High and Low Volume Samplers

Many studies[24,30,43,44] have been conducted to collect particulate-bound PAHs using high-volume sampling with glass fiber filters. In this method, up to 100 m^3/hr of air is drawn through 20 x 25 cm glass fiber filters to allow the collection of up to one gram of particulate matter in 24 hours. The advantage of using a high volume sampler is the high flow rate, which allows the collection of milligram quantities of particulate matter in a day. However, certain sampling problems may occur due to the high air flow rate.

In a study by Katz and Chan,[29] airborne particulate samples were collected by a conventional high volume sampler and by an Andersen cascade impactor every month over a period of one year at two sampling sites in Hamilton, Ontario. The results of this study showed that the size-fractionated samples from the impactor contained much higher amounts of soluble organic material than the corresponding extracts from the Hi-Vol samples. Substantially higher levels of PAHs were also found in the cascade impactor samples. It is reasonable to assume that continued air sampling flow rates of 100 m^3/hr through glass fiber filters over 24 hours may result in a loss of PAHs by sublimation or vaporization from the particulate matter deposited on the filter surface.

Handa and coworkers[30] measured the atmospheric levels of PAHs and the concentrations of particulate matter with various particle size ranges at several sites in Tokyo. A high volume sampler was used to collect air particulate matter, and measurements were made on the particulate material to determine the concentrations of pyrene, chrysene, BaP, and perylene. The

concentration of particulate matter, ranging in size from 0.1 μm to 0.2 μm, was determined with an optical counter. Poor correlations between the quantities of PAHs and of particulate matter were observed. To improve the capture of the missing four-ring PAHs (e.g., pyrene, fluoranthene), an improved collection system with traps cooled by liquid nitrogen was developed. The results showed that 13 percent of total BaA, 17 percent of total chrysene, and 54 percent of pyrene were recovered in the second part of the sampling system.

The sampler EPA(31) has developed to collect the total quantity of pesticidal compounds in air may be used to improve the capture of PAHs. The device uses a high volume sampler to collect particulate matter and a solid sorbent cartridge to trap vapors.

There are few citations describing the use of low-volume (Lo-Vol) samplers. A Lo-Vol sampler has a flow rate about one tenth that of a Hi-Vol sampler. However, only a few studies were found in the literature that used a Lo-Vol sampler to collect ambient air particles, and no study was found that evaluated the distribution of PAHs between vapor and particulate phases. Hence, the comparison of breakthrough values for Hi-Vol and Lo-Vol samplers cannot be addressed. Due to its lower flow rate, breakthrough problems may be less important in a Lo-Vol than in a Hi-Vol sampler. The limited flow rate, however, also limits the sample size, which could be the reason for the few applications of Lo-Vol samplers in ambient air studies.

Grimmer and colleagues(32) used a Lo-Vol air sampler with a glass fiber filter to collect PAHs in air in different areas of an industrial city of 700,000 inhabitants: Essen, West Germany. In Grimmer's study, the samples were collected using a Lo-Vol sampler at the following four selected sites that were polluted by various emissions:

(1) Residential coal heating
(2) Oil heating
(3) Car traffic in a tunnel
(4) Coke ovens.

The PAH concentration profiles were generated using benzo(e)pyrene as a reference compound. BeP concentration was defined as one, and other PAHs were given in ratio to BeP. However, since no absolute concentrations were reported in this study, the comparison of PAH concentrations between Hi-Vol and Lo-Vol samples cannot be addressed here. The results did indicate that the PAH profile differed in many cases from area to area. Cyclopenta(c,d)-pyrene was the predominant species measured in the traffic areas, but was found to be a minor component in the other areas. The author suggested that the different PAH profiles may be helpful to recognize the sources of air pollution.

Impaction Devices

Impaction devices collect and retain particles from an aerosol stream on a surface. Some loss of large particles occurs with high aerosol velocities. It is believed that nearly all small particles of several micrometers or less are retained on the impactor surface.

Several impaction devices have been used in ambient air sampling to collect air samples in different particle size fractions. For example, a cascade impactor and an Andersen sampler are both multi-stage impactor devices. The greatest limitation of the Andersen sampler is its relative low flow rate, one cubic foot per minute. To overcome the low flow rate of the Andersen sampler, a modified Andersen sampler has been devised.(33) The Andersen cascade impactor fractionates particles in a series of six collection stages according to the aerodyamic dimensions of the particles. The modified sampler can operate at a flow rate of 5-6 cfm with removal of the sixth stage of the Andersen sampler; a 4-inch diameter filter is placed downstream to collect the small unimpacted particles. The particle size distributions of suspended particulate matter in six urban areas were determined with this modified sampler.(33) The results indicated that suspended particulate matter in urban air was predominately in the submicron size range. No PAH measurements were performed.

Another size-fractionating particulate sampler consists of a typical Hi-Vol blower unit with an adapter comprised of four stages with successively small slit openings. Behind each slit is a collection plate for retaining particles. The small particles passing through this impaction device are collected using a typical Hi-Vol sampler.

The Institut fur Lufthygiene in West Germany uses two devices known as the BAT I and BAT II to collect ambient air samples.(28) The BAT I and BAT II are similar to a high volume sampler, except that particles larger than 10 µm are removed before passage of the air sample through the BAT I and BAT II system. Only respirable particles are collected by the system. The air flow rate of the BAT I is 10 m^3/hr; that of the BAT II is 100 m^3/hr.

Filter Media

A variety of materials has been used to filter air particles, including cloth,(34) metal fibers,(35) paper,(36) molecular membranes,(37) and glass fibers. Glass fiber filters are widely used in ambient air sampling because these filters have a collection efficiency of a least 99.9 percent for particles of 0.3 µm and larger, low resistance to air flow, and low affinity for moisture. However, several problems with the use of glass fiber filters to collect PAHs in air have been identified by different groups.(6,7,8) All the authors agree that PAHs collected on glass fiber filters show breakthrough problems during long sampling periods. Konig, Cavarkers and coworkers(7) found that during long collection periods, the more volatile PAHs show significant losses; for example, 78 percent of fluoranthene was lost during a 12 week collection. The evaporation of these PAHs is demonstrated by comparing the reentrainment on subsequent filters. The losses can be considerably reduced when the filters are impregnated with glyceroltricaprylate. Loss of fluoranthene was reduced to 13 percent during a 12 week collection when the filters were treated this way. However, only a few studies have investigated the effect of filter materials on collected PAHs. Lee's group(8) has evaluated various candidate filter materials such as glass fiber, quartz fiber, microglass fiber with Teflon binder, and Teflon membrane filters. The evaluation was performed by spiking BaP onto filters two different ways:

(1) Directly spiking ^{14}C-labelled BaP solution onto clean filters or air particulate filter samples, followed by exposure to filtered urban air.

(2) Spiking ^{14}C-BaP onto clean filters or air particulate samples, followed by storage at room temperature in darkness.

In both experiments, better recovery of ^{14}C-BaP was observed using Teflon-coated and Teflon membrane filters compared to glass or quartz fiber filters.

Another study was conducted by Battelle[38] to evaluate five filter types for collection effectiveness for particulate PAHs from diluted diesel exhaust. The filters tested were glass fiber, silanized glass fiber, Pallflex TX 40-HI-20-WW, Pallflex T60A20, and prototype Teflon filters. The results indicated that the filter type does not strongly influence the quantity of PAHs in the collected particulate material. It is noteworthy that the glass fiber filters produced no decrease in the PAH concentrations and appeared to function as well as, and in some cases better than, Teflon-coated filters. It would be worthwhile to compare different types of filters such as glass fiber and Teflon-coated filter material for collecting of PAHs in ambient air sampling.

Adsorbent Media

Several adsorbent materials that have been considered for trapping of PAH vapors are the following:

(a) Tenax-GC
(b) Chromosorb 101
(c) XAD-2
(d) polyurethane foam.

Cautreels and VanCauwenberghe[39] used a Tenax-GC adsorption column mounted after a filtration Hi-Vol sampler to measure pollutants present either as gases or resulting from evaporation of the collected sample. Primarily the lower aliphatic compounds (up to n-docosane and lower homologs), the lower fatty acids (up to pentadecanoic acid), PAHs (up to 4 rings), and methylated derivatives of these compounds are found on the adsorption column. However, Tenax-GC is expensive and requires lengthy purification procedures before use. Also, it has been known to degrade to several diphenylquinones if exposed to hot, oxidizing climates such as those in stack gas emissions.[40] Both XAD-2 and Tenax-GC have been shown to have a high collection efficiency for PAHs.[45,46]

XAD-2 and Chromosorb 101 are both styrene-divinylbenzene copolymers in pellicular form and differ only in particle size. XAD-2 is available in 40/60 mesh, whereas Chromosorb 101 is available in 60/80 mesh. XAD-2 can be a better choice than Chromosorb 101 because the large particle size of the XAD-2 produces a lower pressure drop across the trap, thus permitting a higher sampling flow rate.

Lindgren's[41] group compared two adsorbents (polyurethane plugs and Bondpack-C_{18} plugs) for the collection of PAHs in ambient air. In this study, glass fiber filters were not used to collect particulate matter; only polyurethane plugs and/or Bondpack-C_{18} plugs were used as the collection devices. The polyurethane plugs were found to produce a large amount of extractable UV-absorbing material, which contaminated the air sample during extraction and made the chemical analyses difficult. The Bondpack-C_{18} plugs demonstrated a large resistance to air flow. However, the ease of desorption from C_{18} plugs and the minimal contamination problem suggest that C_{18}-bound adsorbents may provide a viable alternative to the use of polyurethane plugs.

Recently, some other groups[4,5,42] have used polyurethane foam plugs as backup traps to collect vapor phase PAHs in ambient air. This work demonstrated that the use of different solvents (e.g. acetone, cyclohexane, and/or petroleum ether) to clean the polyurethane foam before sampling will minimize the contamination problems observed by Lindgren. In Keller and Bidleman's study,[42] high volume air samples were collected in urban and rural locations using a glass fiber filter/polyurethane foam collection train. Most of the three- and four-ring PAHs were found on the trap, while the higher ring PAHs were retained by the filter. This study also indicated that temperature is the most important consideration in designing collection systems for trace organics. At 20°C and 600 m^3 air, breakthrough to a backup trap was 15 percent for the 3-ring PAHs, phenanthrene and anthracene, and 25 percent for the total organics C_{19}. The same volume of air sampled at 25°C produced breakthrough of 40 percent or more. All the results from these studies showed that polyurethane foams can be useful as adsorbents for PAH vapors because these materials are easy to handle in the field and have good air flow characteristics. No study has been conducted to compare the collection effectiveness and breakthrough values of polyurethane foams with XAD-2. It would be worthwhile to conduct this kind of study to learn which adsorbent is best suited for collecting PAH vapors in ambient air sampling.

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SECTION 5

CHEMICAL ANALYSIS METHODOLOGY

INTRODUCTION

Many studies have been conducted to characterize the PAH content in airborne particulate matter by various analytical techniques. In this review, emphasis will be placed on evaluating different analytical and screening methods to identify suitable methods for the U.S. EPA proposed experimental study.

The analytical techniques that have been used to determine PAHs in ambient air include UV absorption spectroscopy, luminescence spectroscopy, thin layer chromatography (TLC), high performance liquid chromatography (HPLC), gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), Fourier-transform infrared spectroscopy (FT/IR), and Fourier-transform nuclear magnetic resonance spectroscopy (FT/NMR). Each method has distinct advantages and limitations. Often methods can be combined to increase the advantages and decrease the limitations for a specific application. A discussion of the different chemical analysis methods is given in the following paragraphs.

CHEMICAL ANALYSIS METHODS

UV Absorption Spectroscopy

From 1960-1970, many studies[1-5] of PAH determinations were performed using UV absorption techniques. Recently, applications of UV techniques for PAH determination have been few, and the UV absorption techniques that have been used are usually coupled with HPLC and/or GC for separation and detection. The UV absorption technique has several disadvantages, including poor sensitivity compared to other techniques such as luminescence, and overlap of spectra for PAH isomers. Many of the quantitative data in the literature for BaP in environmental samples are probably erroneous, especially those data obtained before 1960, due to the interference of benzo(e)pyrene and/or benzo(k)fluoranthene/benzo(b)fluoranthene. Few studies have been conducted using more sophisticated UV methods to fully utilize the potential of UV absorption spectroscopy. For example, low temperature and derivative absorption spectra can offer more information than conventional UV spectra recorded at room temperature. A prototype instrument has been developed[6-9] for the monitoring of PAH vapors in the field with second-derivative UV absorption spectra. This method is independent of sample capacity, light intensity fluctuations, and source energy variations and does not require sample preparation to remove particulate matter prior to analyses.

Hawthorne and Thorngate have also investigated the analysis of a mixture of PAHs with a least-squares data-analysis computer program.[9] This relatively new technique appears to be successful for selected PAH analyses. Although some additional development, optimization, and field evaluation are still necessary before it can be applied to routine analysis for ambient air samples, this technique may be an excellent screening method for micro-environment site selection.

Luminescence Spectroscopy

Numerous studies[10-19] have been conducted using luminescence techniques to determine PAHs in environmental samples. Sawicki[10] has reviewed the early applications of fluorescence in the analysis of polluted air. He found that luminescence can provide greater specificity and sensitivity than UV absorption techniques in the determination of PAHs, although interferences from other compounds, including impurities in standards, can make the analysis of mixtures difficult. Similar problems were identified by another group[17] that indicated that it is difficult to separate benz(a)-anthracene, chrysene, and triphenylene species. Fluorescence methods[20,21] for the determination of single PAH components in mixtures containing interfering compounds are available, and many of these techniques have been applied to identify BaP.

Luminescence cannot often be used alone to identify PAHs in mixtures because choosing a single wavelength that is characteristic of a particular PAH is not possible for all PAHs. Additional problems can occur when measuring PAHs with luminescence techniques in real ambient air samples. Shifts in wavelength maxima are observed in solution measurements as a function of solvent strength. Increased solvent polarity often generates a bathochromic shift (transition). Another problem with solution optical spectroscopy is the quenching effect observed when additional species in solution suppress the fluorescence of the PAH species by intermolecular deactivation. Sawicki and colleagues[22] have observed this phenomenon with nitrobenzene and nitromethane.

An approach[23-25] to minimize these problems is to use the Shpol'skii effect, which involves the resolution of characteristic vibrational fine structure in the luminescence emission spectra of PAHs in frozen solutions in an n-alkane. The main disadvantage of this technique is that analyses are limited to the determination of PAHs which are soluble in the n-alkane. Another problem with this approach, that has been discussed by Shpol'skii and Bolotnikova in a review,[26] is that the multiple site structure frequently observed in Shpol'skii PAH spectra and the quasilinear (sharp line) effect depend on the freezing rate, concentration of the PAH of interest, and the presence of additional impurities.

Another current development in the use of luminescence for the determination of PAHs is the X-ray excited optical luminescence (XEOL) of PAHs in frozen solutions. One group[27-30] applied the XEOL technique to obtain profiles of PAHs in coal, shale, and fuel oil. These investigators indicated that significant improvements in the clean up procedure to isolate PAH fractions or subfractions will be necessary to obtain quantitative data on actual

samples with this technique. However, no study has been conducted using this technique to determine PAHs in ambient air samples.

Another relatively new technique is luminescence analysis using selective laser excitation. Brown and coworkers[31-33] conducted several studies involving the determination of PAHs by laser-induced fluorescence line-narrowing spectrometry (FLNS) in glassy matrices. They analyzed a solvent-refined coal sample without sample preparation by using two different techniques, GC/MS and FLNS, and quantified three PAHs: pyrene, benzo(e)pyrene, and benzo(a)pyrene. The GC/MS and FLNS data were 1030 ppm and 830 ppm for pyrene, 29 ppm and 56 ppm for BeP, and 84 ppm and 95 ppm for BaP, respectively. However, when HPLC cleanup was used before analysis, both the FLNS and GC/MS determination of pyrene yielded values four times higher (i.e., 4000 ppm). The authors could not provide a reasonable explanation for this discrepancy. Other studies[34-36] have also been conducted using laser-induced luminescence for the determination of PAHs. In general, studies indicate that this technique needs more evaluation and development before it can be used for routine analysis of ambient air samples.

Recently, Vo-Dinh's[37,39-47] group conducted a series of studies to evaluate room temperature phosphorimetry (RTP) and synchronous luminescence (SL) spectrometry techniques for the determination of PAH in environmental samples. Conventional methods in phosphorimetry usually involve the preparation of oxygen-free solutions and the use of rigid matrices of frozen organic solvent to avoid intermolecular deactivation. These techniques involve time-consuming preparation and special experimental devices. RTP is a relatively new technique, which can be used to detect the phosphorescence emitted from organic compounds adsorbed on solid substrates such as silica, alumina, and filter paper at room temperature. Vo-Dinh's group[37,40,42] devoted extensive efforts to developing the use of RTP as a rapid, simple tool for monitoring PAHs in fossil fuel and coal conversion products. The same group also evaluated the use of heavy atom effects to increase the phosphorescence intensities of specific compounds.

The work of Vo-Dinh and his colleagues[41] with synchronous luminescence involved the characterization of naphthalene derivatives in waste water from a coal conversion process. In the synchronous fluorescence techniques, the excitation and emission wavelengths are scanned at the same time with a constant wavelength interval between them, which produces simplified spectra of PAHs. However, Latz and coworkers[38] pointed out the limitations of synchronous luminescence in multicomponent analyses. The results indicate that qualitative surveys can be in error because of wavelength coincidences and/or weak fluorescence signals. For example, the largest peak in the spectrum was attributed to an anthracene concentration of 1 g/ml with only a small contribution from 40 g/ml phenanthrene which had its strongest peak at the same wavelength. The loss of spectral information when the synchronous technique is used can cause misleading results. Vo-Dinh and coworkers[43-47] also applied RTP and SL together as rapid screening tools for monitoring PAHs in environmental samples. In one study.[46] RTP and SL were used to determine PAHs in extracts of a particulate material sample collected on XAD-2 resin. The authors found that fluorimetric and phosphorimetric techniques are complementary in their capabilities for PAH measurements. Anthracene was

easily detected by SF but could not be observed by RTP. BaP can be quantified with SF while the RTP emission of the compound is disrupted by the intense emission from pyrene. With more development and evaluation, SL and RTP techniques can probably be applied for rapid screening of selected PAH compounds in ambient air samples. It is recommended that progress on this work be followed.

Thin Layer Chromatography (TLC)

Several investigators(48-67) have used TLC to separate PAHs and PAH derivatives in ambient air particulate extracts, followed by UV absorption and/or fluorescence spectrometry analyses. In general, TLC techniques are simple, rapid, and less expensive than other separation methods. The main disadvantage of TLC separation is that some active PAHs may adsorb onto an active surface such as alumina and decompose. Elution problems may also occur if compounds bond strongly to the adsorption surface.

For TLC separations, no single method is generally superior to another. The choice of mobile and stationary phases depends on the matrix of the mixture. For example, in one study(48) a cellulose acetate adsorbent system gave best results for the separation of the benzopyrene fraction obtained in column chromatography (i.e., BaP is completely separated from B(k)F, BeP, and perylene). The cellulose adsorbent system gave the best results for the separation of the PAHs. The greatest range in retention values (RB-values) was obtained with a cellulose adsorbent.

Sawicki's group(48-54) have used TLC techniques extensively for the determination of PAHs and their derivatives in various samples (e.g., ambient air particulate matter, coal-tar pitch). They developed a simple method(50) which allows a direct fluorescence analysis of TLC spots. The same group(54) also applied various quenching effects in TLC for determining PAH derivatives. In this study, eight fluorescence quenching techniques were used in the direct analysis of spots on TLC plates. By using these techniques, the following compounds were identified in ambient air particulates: benz(a)acridine, benz(c)acridine, 7H-benz(d,e)anthracenone, benzo(f)quinoline, benzo(h)quinoline, phenalen-1-one, and xanthen-9-one.

Two dimensional development(56,65,66,68) in TLC has been applied and is particularly valuable for complex mixtures such as extracts of airborne particulate material and/or diesel exhaust particulate material. With this technique, the sample extract is applied to the TLC plate and is developed in one direction. Then the plate is rotated through 90° and developed in the second direction. The solvents are varied in these two developments, so different separation effects are obtained in the second dimension. After separation, spots are extracted and determined by fluorescence spectrophotometry.(56,65,66) Recently,(68) a direct fluorescence analysis has been used after two-dimensional TLC chromatography.

In conclusion, TLC techniques have been widely used for the separation of PAHs, even though more efficient and automated systems are available, such as HPLC or GC. This can be attributed to the simplicity of operation and the

reasonable detection limit of TLC.[59] With proper applications, such as the selection of stationary and mobile phases based on the nature of air particulate, TLC can be a reliable method for screening PAHs in extracts of ambient air particulate material.

High Performance Liquid Chromatography (HPLC)

Recently, high performance liquid chromatography (HPLC) has been widely applied for the determination of PAHs in environmental samples.[70-97] The majority of PAH determinations conducted by HPLC involve the use of an octadecylsilane-coated (C_{18}) reverse-phase packing material. Numerous C_{18} materials are commercially available which differ significantly in selectivity characteristics for PAH. Wise and coworkers[86] have evaluated the retention and selectivity characteristics for PAHs on several commercial C_{18} columns. The authors indicated that the BaP/BeP selectivity ratio for one specific commercial C_{18} column was significantly greater than that for any of the other columns evaluated in their study, but the authors did not identify the brand of this tested column.

UV monitors and fluorescence detectors are both widely used in HPLC analyses. Usually, the less expensive UV detectors are employed in analyses requiring a fixed wavelength within the range of 250-280 nm. Recently, several studies[72,76,79,94] have used variable wavelength UV and fluorescence detectors in series. With this technique, PAHs that are not sensitive to UV detection are detected by the fluorescence detector, and those PAHs that are not amenable to fluorescence detection are monitored by the UV detector, producing a significant increase in sensitivity.

Several other types of detectors have been used in HPLC analyses. One group[89,90] recently developed a two-dimensional fluorimetry detector which seems promising, although this system has not been used to analyze PAHs in ambient air. In another study,[91] room temperature liquid phosphorescence detection was used with HPLC to determine PAHs. This technique does not appear useful since, compared to fluorescence detection, the phosphorescence was weak and difficult to obtain.

No reference has been found describing the use of synchronous fluorescence (SF) detection with HPLC for the determination of PAHs in ambient air. One group[92] used reductive electrochemical detection with HPLC to detect nitro PAHs in diesel extracts. By comparing retention times and hydrodynamic voltammograms of unknown peaks with those of reference nitro PAHs, the authors confirmed the presence of 1-nitropyrene in diesel extracts.

For complex matrices such as synthetic fuels or airborne particulate material, HPLC can be used as a preparative procedure to initially[21] fractionate the sample. Analytical scale HPLC or GC is then used to identify and quantify the PAHs.[87,95,96,114]

Tomkins and colleagues,[95] using a semi-preparative scale normal phase HPLC procedure, separated a wide variety of sample types (air particulate matter, coal fly ash and crude oils) into fractions. The fraction with three-

through six-ring PAHs was then analyzed by reversed phase HPLC with fluorescence detection or by GC with flame ionization detection. The authors claimed that the method offers a more rapid and facile approach than traditional procedures involving solvent partitioning and column chromatography in the isolation step. However, some of the PAHs showed poor recoveries from the fractionation scheme, indicating that preparative HPLC would not be useful in every application.

Another method developed by Sonnefeld and coworkers(93) was on-line coupling of a normal phase HPLC system to a reverse phase HPLC system. The on-line coupling system consists of a diamine column for on-column concentration of a selected fraction from a normal phase column separation and a solvent-exchanged procedure using a mobile phase of 40 percent acetonitrile in water transferring the analyte species from the concentrator column onto the head of a guard column. The analyte species were then transferred from the guard column to a reversed phase column by using gradient elution. This on-line multidimensional system produced repeatable determinations of PAH in complex mixtures. These workers also found that an increase in the recovery of most of the PAHs studied could be obtained when the concentration system was purged at ambient temperatures without heating the concentrator column. This procedure, however, required a longer purging time. In addition, certain PAHs were lost in the system and could not be recovered. The extent of this problem must be determined before this HPLC method can be used to obtain quantitative information.

In general, HPLC with UV and/or fluorescence detection can be used for the determination of PAHs in ambient air. Depending on the nature of the mixture, HPLC analysis can be conducted without sample clean-up, choosing optimum detection conditions. The semi-preparative and/or on-line HPLC fractionation can be an alternative to the classical solvent partition/adsorption column chromatographic procedure. However, these techniques still have some limitations such as incomplete recovery of PAHs and limited size of samples which can be generated (100 mg). More studies are therefore required to evaluate and improve these methods, before they can be applied to routine analyses of ambient air.

Gas Chromatography (GC)

Several studies(98-110) have been performed involving the determination of PAHs in ambient air particulate samples and diesel exhaust samples by capillary column GC. The results of these studies demonstrate that capillary GC can be used as a routine analytical tool for the determination of PAHs. However, a sample clean-up procedure is required to remove the interfering compounds such as aliphatic hydrocarbons.

Bjørseth(107,108) conducted several studies of the determination of PAHs in workplace atmospheres. He concluded that the best stationary phase, from the aspects of separation efficiency, column bleeding, and long-term stability, was SE-54. Lee and coworkers(111) conducted a GC retention index study to develop a retention index system for programmed temperature runs, using naphthalene (200.00), phenanthrene (300.00), chrysene (400.00), and picene (500.00) as retention standards. The average 95 percent confidence

limits for four measurements on more than 200 compounds were ±0.25 retention index unit. The authors indicated that even column-to-column variations were unimportant when using this retention measurement approach.

Several detectors are used in gas chromatography, including UV,(100,101,104) fluorescence,(106,113) flame ionization (FID),(98,99,103,107, 108,110,111) and electron capture.(112) The UV and fluorescence detectors, used in a stopped-flow mode with the addition of solvent, were used in earlier PAH determinations. The flame ionization detector (FID) is now universally used for PAH determinations. The advantages of FID are linear response, sensitivity, and day-to-day quantitative reliability in routine determinations. Typical detection limits for PAHs are below 1 ng; different detector designs and instruments can cause some variations in this limit.

With proper sample preparation procedures to isolate a PAH fraction from complex mixtures of ambient air extracts, the capillary column GC/FID technique can be used for the routine determination of PAHs. Recently, a study(114) was conducted to determine nitrated PAHs in ambient air samples using GC with a nitrogen-selective detector. In this study, a method was developed for isolating PAHs and their nitro derivatives by normal phase HPLC. The nitrated PAH fraction was analyzed by GC with nitrogen selective detection (NP detector). Compounds identified in airborne particulate matter included 9-nitroanthracene, 1-nitropyene, and 10-nitrobenz(a)anthracene.

It would be worthwhile to conduct a series of studies for the determination of nitrated PAHs using GC with electron capture detection, Hall detection in the nitrogen mode, and/or NP detection to address the possibility of using GC for the routine determination of nitrated PAHs. It should be noted that single column/single detector GC and HPLC have only weak specificity, and confirmation of compound identifications made by these techniques is necessary.

Gas Chromatography/Mass Spectrometry (GC/MS)

Numerous applications using a GC/MS technique for determining PAHs in air particulate matter were found in the literature.(115-122) The advantages of this technique are high sensitivity for trace level detection, specificity for unequivocal identification, and versatility for the separation of large numbers of compounds. The main disadvantage is that it is significantly more expensive than GC/FID, HPLC/UV, fluorescence, or other techniques. For most studies, the mass spectrometer was operated using either full scan or selected ion monitoring (SIM) modes. A recent study(113) used GC/MS in the SIM mode to quantify five PAHs in diesel exhaust particulate material. In the SIM mode the mass spectrometer concurrently monitors one or more ion peaks, characteristic of a specific compound, during its expected elution time from the gas chromatographic column. Because the ion peaks that are monitored are specific to the PAH compounds being analyzed, ion peaks from other compounds at non-monitored masses will not contribute to the monitored ion current signal. Therefore other compounds will not interfere with the analysis, and SIM will enhance the sensitivity compared to the full scan mode. The quantification limit of this procedure was 175 pg of selected PAHs injected on the GC column.

Recently, Battelle developed a gas chromatography/negative ion chemical ionization mass spectrometric (NCI, HRGC/MS) method using on-column injection to identify and quantify nitro PAHs in extracts of diesel exhaust particulate material and air particulate material.(122,124) The NCI technique provides up to a 100-fold increase in sensitivity and selectivity, compared to conventional chemical ionization, for detection of nitro PAHs. The on-column injection method provides significant benefits for the analysis of nitroaromatics over the conventional heated injection port methods. Nitrated PAHs, especially dinitropyrenes, are thermally labile and will decompose at injection port temperatures necessary for sample volatilization. With the NCI GC/MS on-column injection technique, the sample can be injected into the chromatographic system at a lower temperature (e.g., 40°C) to eliminate degradation of the thermally labile nitroaromatics. Chemical ionization is much less energetic than electron impact, which increases the ionization efficiency and thus enhances the detection sensitivity. This is due to the electronegative nature of the nitro substituent, which is highly susceptible to attachment of a thermal electron from the reagent gas plasma. For the reasons listed above, the NCI on-column injection GC/MS method is the most sensitive and selective method for the determination of nitro PAHs. The quantification limit for several nitro PAHs using this method is 0.1 ng on the column.

For the future U.S. EPA experimental study, both EI GC/MS and NCI GC/MS techniques can be used for determining PAHs and nitro PAHs respectively.

Fourier-Transform Nuclear Magnetic Resonance (FT-NMR) and Infrared Spectroscopy (FT-IR)

Both FT-NMR and FT-IR have been used to determine PAHs in various matrices. Wehry and coworkers(125-128) have conducted detailed investigations of the applicability of matrix isolation (MI) FT-IR in the qualitative and quantitative determination of PAHs. In one study,(126) these workers demonstrated the application of this technique to the identification of PAHs of coal-derived materials.

Bartle and coworkers(129) identified methyl derivatives of PAHs in air particulate material and in tobacco and marijuana smoke condensates with FT-NMR. The analytical method involved separating sample condensates into fractions of similar ring types with chromatographic techniques and determining PAH compounds in the fractions with FT-NMR. The positions of substitution in the rings were identified from the methyl chemical shifts in the FT-NMR spectra. The authors indicated that for the lower relative molecular mass fractions of anthracene-phenanthrene and fluoranthene-pyrene the smaller number of methyl derivatives makes identification possible from FT-NMR spectra alone.

For the determination of PAHs in ambient air, both FT-IR and FT-NMR techniques are not practical. Both techniques require larger sample sizes than other techniques (HPLC, GC, and/or GC/MS). Also, the identification of PAHs in mixtures is difficult with both FT-IR and FT-NMR techniques. However, both FT-IR and FT-NMR can be useful tools for determining the structure of unknown PAHs.

SCREENING METHODS

Based on the review of available analysis methods for the determination of PAHs in ambient air samples, several screening methods are selected for possible application in the future EPA experimental study and described in the following sections.

Sensitized Spot Test

A screening procedure based on naphthalene-enhanced fluorescence has been extensively validated by the U.S. EPA Industrial Environmental Research Laboratory at the Research Triangle Park, North Carolina.(130-133) In the enhanced fluorescence spot test, a portion of the sample extract is transferred to filter paper along with a highly concentrated naphthalene solution. After solvent vaporization, the unknown molecular species are entrained in a crystalline naphthalene matrix. In the naphthalene matrix, the native PAH analytes are excited by vibrational coupling with the more energetic excited states of the naphthalene to produce an enhanced fluorescence. This enhanced fluorescence is easily detected visually. For selected compounds, e.g., fluoranthene, a sensitivity of 10 pg was reported for this spot test.(132) Two interferences were observed(131) in the spot test: highly colored samples restricted viewing of the fluorescence level, and samples containing substantial amounts of phthalate esters produced false positive results. No false negative results were observed in this study. The color interference problem can be easily eliminated by diluting the sample. However, the false results obtained with phthalate esters are not as easily reconciled and can pose a major deterrent for using the spot test to screen samples for content PAH. A Battelle study(122) has identified phthalate esters as the major component in the polar fraction of air particulate material. The phthalate ester interference problem must be evaluated before the spot tests can be used as a screening method for the determination of PAHs in ambient air. Nevertheless, this technique is inexpensive, simple, and rapid and should be useful as a screening procedure to identify samples to be carried forward for more expensive analyses.

UV Spectroscopic Method

A surrogate method(134) for the determination of total PAH concentration (fluoranthene equivalents) in industrial effluents was developed by Battelle. This method employed solvent extraction, alumina column chromatographic cleanup (optional), and UV absorbance determination. The UV detection step utilized a bandpass filter in order to obtain more uniform response between the various PAHs. In this method, the matrix can produce interferences that are coextracted from the sample. The extent of these interferences varies and depends upon the nature and diversity of the matrix. A cleanup procedure can be used to overcome the interferences, but the cleanup procedure will offset to some extent the simplicity of the method. Nevertheless, with modifications and evaluation, the UV spectroscopic method may be very useful as a screening method to determine PAHs in ambient air.

TLC Procedure

Many studies (discussed in an earlier section) have used TLC with UV or fluorescence detection for the determination of PAHs in ambient air samples. TLC is rapid, reproducible, and inexpensive, and can be employed as a screening method. One group(135) separated BaP from other chemical species using an acetylated cellulose substrate and optical isolation of BaP by direct reflectance fluorescence from the TLC plate. This group was able to accurately screen 30-40 samples per day for BaP using this technique. A screening TLC procedure can be developed for the measurements of selected PAHs in the future experimental study.

Luminescence Technique

As mentioned in an earlier section, Vo-Dinh's group has investigated synchronous fluorescence (SF) and room temperature phosphorescence techniques for PAH determinations. However, few of their studies involved ambient air samples. These techniques are applicable as screening tools for PAH measurement in ambient air samples; however, further investigations and evaluations are needed.

Recently, Battelle (136) studied the use of a pulsed tunable-dye laser system to conduct fluorescence/phosphorescence measurements of PAHs. This technique also has potential as a screening method in ambient air study, but further studies are needed to evaluate the possibility of the use of this system to obtain direct fluorescence and/or phosphorescence measurements on the filters.

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